Synthesis and Structures of an Organometallic Carboxyphosphine, *rac*-{2-(Diphenylphosphino)ferrocenyl}acetic Acid, Related Compounds, and Palladium(II) Complexes with *rac*-{2-(Diphenylphosphino)ferrocenyl}acetato or Methyl *rac*-{2-(Diphenylphosphino)ferrocenyl}acetate and Ortho-Palladated *C,N*-Chelate Ligands

Petr Štěpnička* and Ivana Císařová

Department of Inorganic Chemistry, Charles University, Hlavova 2030, 128 40 Prague 2, Czech Republic

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An organometallic carboxyphosphine, *rac*-[2-(diphenylphosphino)ferrocenyl]acetic acid (*rac*-Hpfa*), was synthesized from *rac*-*N*,*N*-dimethyl[2-(diphenylphosphino)ferrocenyl]methylamine by successive alkylation to *rac*-benzyldimethyl{2-[(diphenylphosphino)ferrocenyl]methyl}-ammonium bromide (**2***), a replacement of the ammonium group with CN^-, and, finally, hydrolysis of the obtained *rac*-[2-(diphenylphosphino)ferrocenyl]acetonitrile (**3***). The acid was further converted to the respective methyl ester **4**, phosphine oxide **5***, and phosphine sulfide **6***. The metathesis of the in situ generated salt *rac*-Kpfa with di-μ-chloro-bis{2-[(dimethylamino)methyl-κN]phenyl-κC^1}dipalladium(II) (**7**) afforded a heterobimetallic complex with the chelating carboxylate pfa$^-$-$\kappa^2 O,P$ and the cyclometalated C,N-ligand, [*SP*-4-3]-{2-[(dimethylamino-κN)methyl]phenyl-κC^1}{*rac*-[2-(diphenylphosphino-κP)ferrocenyl]acetato-κO^1}palladium(II) (**8***), while the cleavage of the chloro bridges in **7** with **4** gave a complex with a P-bonded phosphino ester, [*SP*-4-4]-chloro{2-[(dimethylamino-κN)-methyl]phenyl-κC^1}{*rac*-methyl [2-(diphenylphosphino)ferrocenyl]acetate-κP}palladium(II) (**9***). Compound **9** was further converted by reacting with $AgClO_4$ to the cationic bis(chelate) complex [*SP*-4-3]-{2-[(dimethylamino-κN)methyl]phenyl-κC^1}{*rac*-methyl [2-(diphenylphosphino-κP)ferrocenyl]acetate-κO^2}palladium(II) perchlorate (**10***). Complex **10** was alternatively obtained by a replacement of acetonitrile ligands in bis(acetonitrile){2-[(dimethylamino)methyl]phenyl-$\kappa^2 C^1,N$}palladium(II) perchlorate (**11**) with **4**. (The asterisk indicates that the solid-state structure has been determined by X-ray crystallography.)

Introduction

Phosphinocarboxylic acids, owing to the presence of hard and soft donor groups[1] and their chemical properties, constitute a specific class of versatile hybrid ligands capable of coordinating in very diverse donor modes to almost any metal (P, O, and combined coordination, protonated or dissociated carboxyl group, formation of chelates and bridges, etc.).[2,3] Of particular importance is hemilabile coordination of these ligands to soft metals typically used in catalysis, where the weakly coordinating hard group protects a vacant coordination site in a catalytic intermediate.[4]

The very basic phosphinocarboxylic compound (diphenylphosphino)acetic acid[2] is an archetypal ligand for nickel-catalyzed oligomerization of ethene, which represents the key step of the Shell higher olefin process.[5] Palladium complexes of the acid, its homologues, and the respective esters $Ph_2P(CH_2)_nCO_2R$ (n = 1−3, R = H, Me, Et), were applied as catalysts in codimerization of ethene and styrene and in co-oligomerization of ethene with CO,[6] while palladium complexes obtained from the deprotonated ester $Ph_2PCH_2CO_2Et$ were shown to reversibly activate CO_2.[7] The presence of the carboxyl group or its dissociated form results in an increased

* To whom correspondence should be addressed. E-mail: stepnic@mail.natur.cuni.cz.

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solubility of phosphinocarboxylic ligands in polar solvents, allowing homogeneously catalyzed reactions to be performed even in water.[8] The ligands $R_{3-n}P(CH_2CO_2H)_n$ ($n = 1-3$, R = Me, Et, Ph) have also been tested as extractants for the recovery of platinum metals from reaction mixtures after catalytic transformations.[9] Furthermore, a recent demand for ligands enabling metal-catalyzed transformation to be performed in a stereoselective manner prompted the preparation of some chiral phosphinocarboxylic acid: the acids so far synthesized were derived from C-chiral organic backbones, and their activity has usually been assessed in enantioselective palladium-catalyzed allylic alkylation.[10]

Considering the vast number of ferrocene ligands and the unique stereoelectronic and electrochemical properties of the ferrocene framework,[11] it appears rather surprising that although many potential O,P-hybrid ferrocene ligands—for instance ferrocene phosphino alcohols and their esters and phosphino ethers,[12] phosphino aldehydes and ketones,[13] and some phosphinoamides[14]—are available, only very few of them were tested as ligands in transition-metal complexes. In 1995, we reported the synthesis of a ferrocene carboxyphosphine, 1′-(diphenylphosphino)ferrocenecarboxylic acid (Hdpf)[15] and since then demonstrated its ability to bind transition metals in various modes.[16,17]

A chiral isomer of Hdpf, (S_p)-2-(diphenylphosphino)-ferrocenecarboxylic acid (**I**, HL^1; Chart 1)[18] and derivatives of its more complex analogue, (S_p,S_p)-2,2′-bis-(diphenylphosphino)-1,1′-dicarboxylic acid (**II**),[19] were

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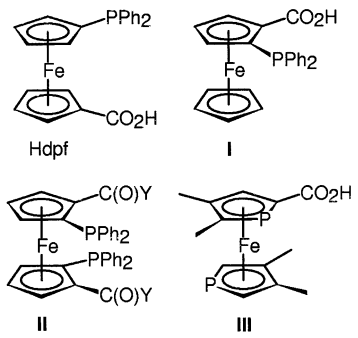
Chart 1



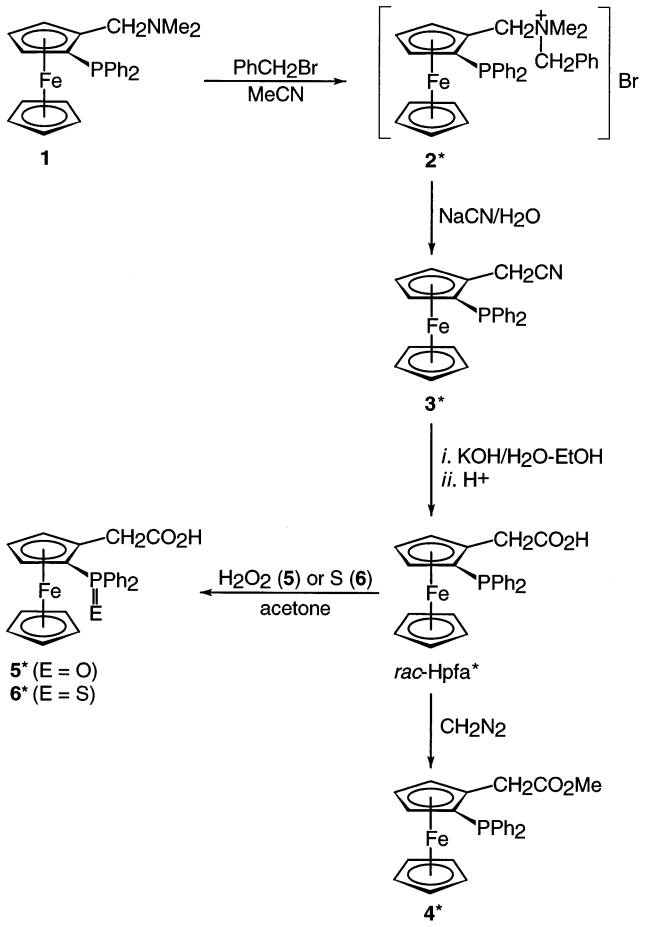
synthesized from chiral phosphinoferrocene oxazolines[20] and used as ligands in allylic alkylation. It was also demonstrated that a deprotonation of the former ligand followed by metathesis with [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] gives a mixture of diastereoisomeric *O*,*P*-carboxylato complexes which undergoes a spontaneous resolution in solution to afford pure (R_{Ru},S_p)-[RuCl(L^1-κ^2*O*,*P*)(η^6-*p*-cymene)].[18c] The epimerization yields the sterically (thermodynamically) preferred diastereoisomer and appears to be facilitated by hemilabile coordination of the carboxylate (L^1)$^-$ (strong Ru−P bond and labile Ru−O bond; cf. the complex *trans*-[Rh(CO)(Hdpf-κ*P*)(dpf-κ^2*P*,*O*)],[16c] where the two forms of the Hdpf ligand rapidly interchange the acidic hydrogen). A recent example of an alternative approach to ferrocene-based, carboxylic *O*,*P*-donors is the carboxylated 1,1′-diphosphaferrocene **III**.[21]

In this contribution, we report the synthesis and structures of a novel planarly chiral but racemic, ferrocene-based carboxyphosphine ligand, *rac*-[2-(di*p*henylphosphino)*f*errocenyl]*a*cetic acid (*rac*-Hpfa), its selected derivatives and palladium(II) complexes with *rac*-[2-(diphenylphosphino)ferrocenyl]acetato or methyl *rac*-[2-(diphenylphosphino)ferrocenyl]acetate and cyclometalated C,N-chelate ligands.

Results

The racemic nitrile **3** was obtained in 72% isolated yield from one-pot alkylation of *rac*-**1** with benzyl bromide and a subsequent replacement of the ammonium group in the alkylated intermediate **2** with CN$^-$ with liberation of *N*-benzyldimethylamine (Scheme 1). The procedure has been proposed by taking into the account a previous report[12a] that **1** reacts with 1 equiv of methyl iodide to give preferably an unstable N-alkylated product, which further reacts with O- and N-nucleophiles in a manner analogous to that for the nonphosphinylated salt [FcCHNMe$_3$]I,[22] while the reaction of **1** with an excess of MeI yields the respective P,N-dialkylated salt. Following the alkylation by NMR spectroscopy revealed that the reaction of benzyl bromide with *rac*-**1** (1:1 molar ratio, in acetonitrile-d_3 at

Scheme 1. Preparation of *rac*-Hpfa and Its Derivatives[a]



[a] The asterisk indicates that the crystal structure has been determined.

25 °C) is completed within 30 min, yielding solely the N-alkylated compound **2**, and that the reaction mixture remains unchanged over 24 h. In ^{1}H NMR spectra, the salt exhibits signals of nonequivalent, diastereotopic methyl groups (unlike the parent amine) which are shifted to a lower field and, additionally, a pair of doublets due to the AB spin system of the benzyl methylene group. The exclusive N-alkylation is best reflected by ^{31}P NMR spectra, which show only one, upfield-shifted resonance (*rac*-**1**, δ_P −22.8; *rac*-**2**, δ_P −27.4). The shift corresponds to a formation of a cationic product with an intact phosphino group; for the case of P-alkylation, a larger shift in the *opposite* direction could be expected (cf. PPh$_2$Me, δ_P −28; [PPh$_2$Me(CH$_2$Ph)], δ_P +22.8).[23]

As the addition of a further 1 equiv of PhCH$_2$Br induced separation of a rusty orange, crystalline solid and thus prevented a further in situ NMR study, the dialkylation was attempted separately by reacting **1** with 2 equiv of benzyl bromide in anhydrous acetoni-

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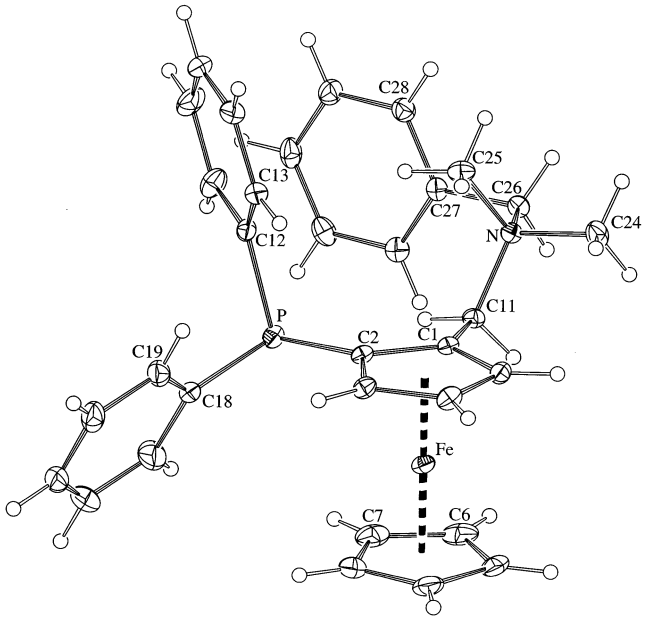


Figure 1. Molecular structure of the cation in ammonium salt **2**. Selected distances (Å) and angles (deg): Fe−ring centroid = 1.6379(8) for C(1−5) and 1.653(1) for C(6−10); P−C(2) = 1.823(2), P−C(12) = 1.837(2), P−C(18) = 1.840(2), N−C(11) = 1.526(2), N−C(24) = 1.501(2), N−C(25) = 1.493(2), N−C(26) = 1.536(2), C(1)−C(11) = 1.497(3), C(26)−C(27) = 1.506(2) Å; C−P−C = 101.22(9)−102.68(9), C−N−C = 106.2(1)−111.9(1), C(1)−C(11)−N = 114.7(1); C(11)−C(1)−C(2)−P = 2.2(2); cyclopentadienyl ring tilt, 0.6(1)°. The cations are involved in $\pi-\pi$ stacking interactions of the C(27−32) phenyl rings of neighboring molecules (ring centroid distance 3.587(1) Å) and in weak cation−anion interactions, of which the C(11)−H(11B)···Br^{i} hydrogen bond is the shortest contact (C(11)···Br = 3.7712(2) Å, C(11)−H(11B)···Br = 146°; (i) x, $1 - y$, $z - 2$).

trile. Rather unexpectedly, the crystalline solid which separated from the reaction mixture was characterized by NMR spectroscopy and X-ray crystallography (Figure 1) as the pure *monoalkylated* compound **2** (78% isolated yield at 0.1 mmol scale).

Nitrile **3** was hydrolyzed with potassium hydroxide in an ethanol−water mixture at reflux temperature. A subsequent acidification of the reaction mixture and recrystallization of the crude product gave pure *rac*-Hpfa as a yellow-orange, air-stable crystalline solid in 88% yield. The acid was converted to its methyl ester **4** by reaction with diazomethane in diethyl ether (92% isolated yield) and quantitatively yielded the corresponding phosphine oxide **5** and sulfide **6** by reacting with hydrogen peroxide and sulfur, respectively (Scheme 1). All compounds were characterized by spectral methods (NMR, IR, MS) and elemental analyses. The structures of **2**, **3**, *rac*-Hpfa, **5**, and **6** were determined by single-crystal X-ray diffraction.

Crystal Structures of *rac*-Hpfa, 5, and 6. The molecular structure of *rac*-Hpfa is shown in Figure 2. The pertinent geometric parameters for the acids are summarized in Table 1 along with the data for nitrile **3** (for views of the molecular structures of **3**, **5**, and **6**, see the Supporting Information). At first sight, the structures show no unexpected features and their metric parameters compare favorably to those of Hdpf, 1′-(diphenylphosphinoyl)ferrocenecarboxylic acid,[15a] and ferrocenylmethanol derivatives bearing Ph_2P, $Ph_2P(O)$, and $Ph_2P(S)$ groups in the 2-position of the ferrocene unit.[24] The compounds exhibit neither any significant tilt of the cyclopentadienyl rings (maximum 5.16(9)° for **6**) nor torsion at the C(1)−C(2) bond (maximum 7.2(3)° for **5**). A formal replacement of the lone electron pair at

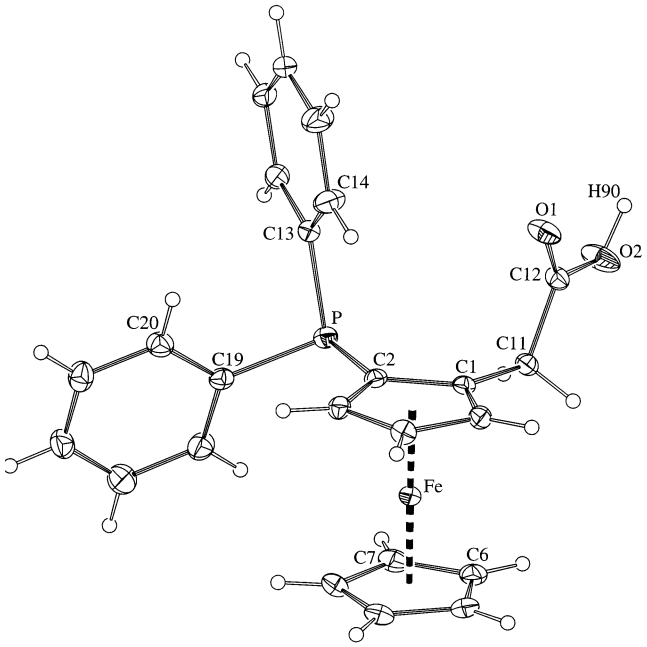


Figure 2. View of the molecular structure of *rac*-Hpfa showing the atom-labeling scheme. Thermal ellipsoids correspond to the 30% probability level.

Table 1. Selected Geometric Parameters for 2, 3, Hpfa, 5, and 6 (values in Å and deg)[a]

	3[c]	Hpfa	**5**[d]	**6**[e]
E	void	void	O	S
Fe−Cg1	1.6462(7)	1.6386(8)	1.6391(9)	1.6443(7)
Fe−Cg2	1.6549(7)	1.6499(9)	1.653(1)	1.6596(7)
C(1)−C(11)	1.504(2)	1.498(2)	1.496(3)	1.505(2)
C(11)−C(12)	1.461(2)	1.506(2)	1.521(3)	1.509(2)
C(12)−O(1)		1.211(2)	1.199(3)	1.251(2)
C(12)−O(2)		1.320(2)	1.299(3)	1.278(2)
P=E			1.496(2)	1.9561(5)
P−C(2)	1.816(1)	1.816(2)	1.783(2)	1.795(3)
P−C(13)	1.835(2)	1.841(2)	1.803(2)	1.812(2)
P−C(19)	1.832(2)	1.836(2)	1.804(2)	1.819(2)
C(2)−C(1)−C(11)	123.5(1)	125.9(1)	125.5(2)	126.4(1)
C(1)−C(11)−C(12)	113.2(1)	114.5(1)	115.2(2)	114.3(1)
O(1)−C(12)−O(2)		123.2(2)	122.1(3)	123.5(2)
C(1)−C(2)−P	123.3(1)	123.8(1)	127.0(1)	125.8(1)
C−P−C[b]	100.45(6)−101.86(7)	100.85(8)−102.33(8)	105.07(9)−107.16(9)	103.42(7)−105.22(7)
C(11)−C(1)−C(2)-P	−6.1(2)	−3.4(2)	7.2(3)	−5.2(2)
Cp1,Cp2	1.75(9)	1.3(1)	1.4(1)	5.16(9)

[a] Distances are given in Å and angles in deg. Atom-labeling schemes are analogous for all compounds. Views of the molecular structures of **3**, **5**, and **6** are available as Supporting Information. Plane definitions (plane, defining atoms [centroid]) for **3**, Hpfa, **5**, and **6**: Cp1, C(1−5) [Cg(1)]; Cp2, C(6−10), [Cg(2)]; Ph1, C(13−18), [Cg(3)]; Ph2, C(16−24), [Cg(4)]. [b] The range of C(2)−P−C(13,19) and C(13)−P−C(19) angles. [c] Further data: C(12)−N = 1.140(2) Å, C(11)−C(12)−N = 178.9(2)°. [d] O(3)−P−C(2,13,19) angles: 110.25(9)−115.68(9)°. [e] S−P−C(2,13,19) angles: 112.91(5)−116.11(5)°.

(24) Štěpnička, P.; Císařová, I. *New J. Chem.* **2002**, *26*, 1389.

phosphorus (*rac*-Hpfa) with oxygen and sulfur (**5** and **6**, respectively) results in opening of the C−P−C angles and shortening of the P−C bond lengths, which can be accounted for, respectively, by the different steric demands of the "fourth" substituent and enhanced Ph → P π-electron density transfer upon introduction of an electronegative atom onto phosphorus.

The geometry of the flexible CH_2CO_2H arms in the acids are very similar, but the orientations of the carboxyl planes C(12)O(1)O(2) toward the adjacent cyclopentadienyl ring Cp1 differ (the respective dihedral angles are as follows: *rac*-Hpfa, 87.4(1)°; **5**, 35.5(5)°; **6**, 69.9(1)°), reflecting likely a different nature of the solid-state interactions in which the molecules are involved. As commonly observed in lattice arrays built up by carboxylic acids, the molecules of *rac*-Hpfa assemble into centrosymmetric dimers via planar, double hydrogen bridges between carboxyl groups of adjacent molecules: O(2)−H(90)···O(1)$^{\&(-x,1-y,1-z)}$ (O−H = 0.96(3) Å, O···H = 1.70(3) Å, O···O = 2.646(2) Å, O−H···O = 172-(3)°). The O···O separation is identical with the value typical for Hdpf and its complexes featuring similar hydrogen bonding patterns (ca. 2.65 Å).[15a,16b,d,e,g] The dimers are packed at the normal van der Waals distances. Acid **6** forms similar hydrogen bridges O(2)−H(90)···O(1)$^{\&(-x,1-y,1-z)}$ (O−H = 0.99(4) Å, O···H = 1.66(4) Å, O···O = 2.649(2) Å, O−H···O = 179(5)°), though, in this case, the solid-state packing is further aided by weak C−H···π hydrogen bonds (C(4)−H(4)···Cg(4)$^{\&(x-1,y,z)}$: H···Cg = 2.77 Å, C···Cg = 3.636(3) Å, C−H···Cg = 156°; see Table 1 for the definition of the least-squares planes).

The molecules of phosphine oxide **5** associate into centrosymmetric, doubly hydrogen bonded dimers as well. However, unlike the above cases the hydrogen bonds involve the carboxyl and phosphinoyl moieties from neighboring molecules (O(2)−H(90)···O(3)$^{\&(2-x,-y,-z)}$: O−H = 0.97 Å, O···H = 1.65 Å, O···O = 2.596(3) Å, O−H···O = 164°). The O···O distance is similar to the distance observed in the structure of 1′-(diphenylphosphinoyl)ferrocenecarboxylic acid (O···O = 2.588(3) Å)[15a] and slightly longer than that in (S_p)-2-(diphenylphosphinoyl)ferrocenecarboxylic acid (O···O = 2.556(4) Å).[18c] A preferential formation of the C(=O)*O*−*H*···*O*=P hydrogen bonds parallels the behavior of 1′-(diphenylphosphino)ferrocenecarboxylic acid and its *P*-oxide,[15a] and the aforementioned series of ferrocenylmethanol derivatives with phosphorus substituents.[24] The tendency of the carboxyl group to form hydrogen bridges to the phosphinoyl oxygen atom apparently reflects the nature of the phosphinoyl group as a better hydrogen bond acceptor than a carboxyl group. In addition to the strong O−H···O hydrogen bonding, the solid-state assembly of **5** is further stabilized by weak C−H···π hydrogen bonds C(22)−H(22)···Cg(3)$^{\&(x-1,y,z)}$ (C···Cg = 3.591(3) Å, C−H···Cg = 160°).

Preparation of Complexes. Metathesis of the chloro-bridged dimer **7** with 2 equiv of *rac*-Kpfa generated in situ by neutralization of *rac*-Hpfa with a stoichiometric amount of *t*-BuOK gave the crystalline heterobimetallic bis-chelate complex **8** in 88% yield after recrystallization (Scheme 2). Complex **7** also reacts cleanly and quantitatively with 2 equiv of ester **4** to give the expected product of a bridge cleavage reaction, the bimetallic complex **9**, which was isolated in 52% yield after recrystallization. A analogous reaction with *rac*-Hpfa affords a complicated mixture from which no defined product could be isolated by crystallization. It is likely that the primary bridge-splitting reaction is in this case accompanied by an acidolysis of the Pd−C bonds and subsequent decomposition steps.

A removal of chloride ligand from in situ prepared complex **9** with silver perchlorate creates a free coordination site, thus enforcing an intramolecular coordination of the carbonyl group of the phosphino ester ligand to furnish the cationic bis(chelate) complex **10** in 90% isolated yield. The reaction proceeds without change of the configuration at the palladium atom. The same product is also obtained by reacting stoichiometric amounts of the cationic bis(acetonitrile) complex **11** and ester **4**. Similarly to its analogues,[25] the precursor complex **11** was obtained as colorless needles by treatment of **7** with 1 equiv of $AgClO_4$ in acetonitrile−dichloromethane and recrystallization from acetonitrile−diethyl ether in 92% yield. Complexes **8**−**10** are rusty orange, air-stable crystalline solids, well-soluble in polar halogenated solvents (CH_2Cl_2, $CHCl_3$).

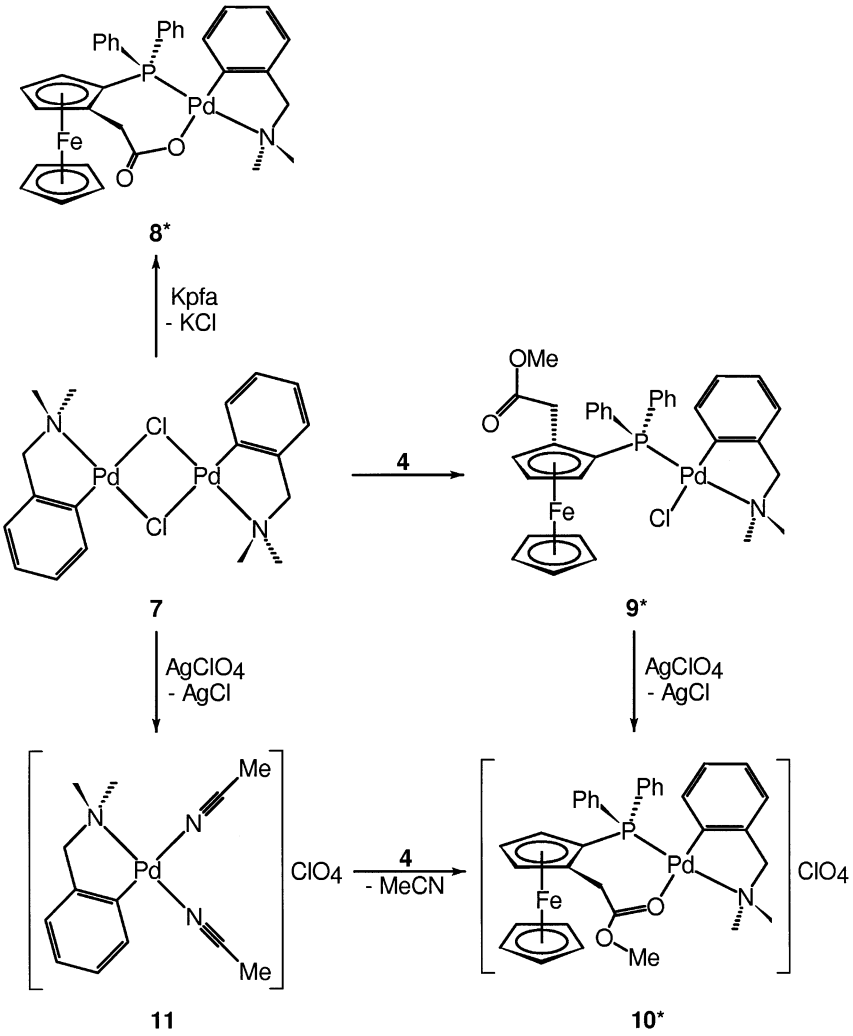
All complexes were characterized by spectral methods and the structures of **8**−**10** further corroborated by single-crystal X-ray diffraction (see below). In NMR spectra, complexes **8**−**10** exhibit distinct signals of the diastereotopic methylene protons (C*H*$_2$N, C*H*$_2$CO$_2$) and methyl (N*Me*$_2$) groups. The $^4J_{PH}$ (cf. ref 26) and $^3J_{PC}$ coupling constants indicate the *trans*-P−N arrangement is maintained in all compounds. In the case of **8**, the P-coordination is reflected by a significant downfield shift in the ^{31}P NMR spectra (by 53.0 ppm vs free Hpfa). As far as the carboxylate part in **8** is concerned, the carbon resonance due to the carboxylate group shows only a small variation compared to the free ligand (δ_C: Hpfa, 176.24; **8**, 175.72) and, hence, the O-coordination is best verified by IR spectra displaying intense composite carboxylate bands at 1580−1622 cm^{-1}, shifted by about 100 cm^{-1} to lower energies with respect to uncoordinated Hpfa. NMR spectra of **9** are in agreement with the anticipated behavior of ester **4** as a simple phosphine (the ^{31}P coordination shift $\Delta_P = \delta_{complex} - \delta_{ligand}$ is 50.9 ppm). The IR spectra of **4** and **9**, which show the carbonyl stretching band at exactly the same position (1734 cm^{-1}), rule out any significant interaction of the palladium center with the ester function (cf. structural data below).

The changes observed on going from **9** to **10** reflect clearly the closure of the chelate ring as well as the formation of the cationic species. A reduced electron density at the donor groups due to an enhanced donation to the electron-poor (cationic) metal center results in low-field shifts of about 3 ppm in ^{31}P NMR and ca. 7 ppm for C=O signal in ^{13}C NMR spectra. The coordina-

(25) (a) Chooi, S. Y. M.; Siah, S.-Y.; Leung, P.-H.; Mok, K. F. *J. Am. Chem. Soc.* **1993**, *32*, 4812. (b) Valk, J.-M.; van Belzen, R.; Boersma, J.; Spek, A. L. K.; van Koten, G. *J. Chem. Soc., Dalton Trans.* **1994**, 2293.

(26) (a) Mathesis, C.; Braunstein, P. *J. Organomet. Chem.* **2001**, *621*, 218. (b) Bouaoud, S.-E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1988**, *27*, 2279. (c) Bouaoud, S.-E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1986**, *25*, 3765. (d) Braunstein, P.; Fischer, J.; Matt, D.; Pfeffer, M. *J. Am. Chem. Soc.* **1984**, *106*, 410. (e) Balegroune, F.; Grandjean, D.; Lakkis, D.; Matt, D. *J. Chem. Soc., Chem. Commun.* **1992**, 1084. See also refs 2f and 7a,b.

Scheme 2. Synthesis of Palladium(II) Complexes with Pfa− and 4 as the Ligands[a]



[a] The asterisk indicates that the crystal structure has been determined.

tion of the carbonyl oxygen also causes a shift of the carbonyl stretching band by about 62 cm^{-1} to lower frequencies. This shift is about 10−20 cm^{-1} lower than the change observed for an analogous system with $Ph_2PCH_2CO_2Et$ as the ligand,[7a] indicating a less pronounced C═*O*→Pd donation in **10**, which is in accordance with the strong electron donating nature of the ferrocenyl group and, consequently, a higher donating ability of the directly attached phosphino moiety. The presence of a perchlorate counterion in **10** is manifested by its very strong, composite absorption bands in IR spectra (ν_3 1110 cm^{-1}, ν_4 624 cm^{-1}).

Crystal Structure of 8. The structure consists of discrete molecules packed at the distances of van der Waals contacts. The molecular structure of **8** is shown in Figure 3, and selected geometric data are given in Table 2. As manifested by the sum of the donor−palladium−donor angles (359.9°) and the maximum deviation from the least-squares plane defined by the four donor atoms and the palladium center (PdL_4; 0.098(2) Å for C(26)), the palladium atom is located in an almost perfectly planar coordination environment. Due to the steric requirements of the ligands and different palladium−donor bond lengths, however, the palladium atom is slightly shifted along the N→P vector toward the phosphorus atom. The palladium−donor bond lengths

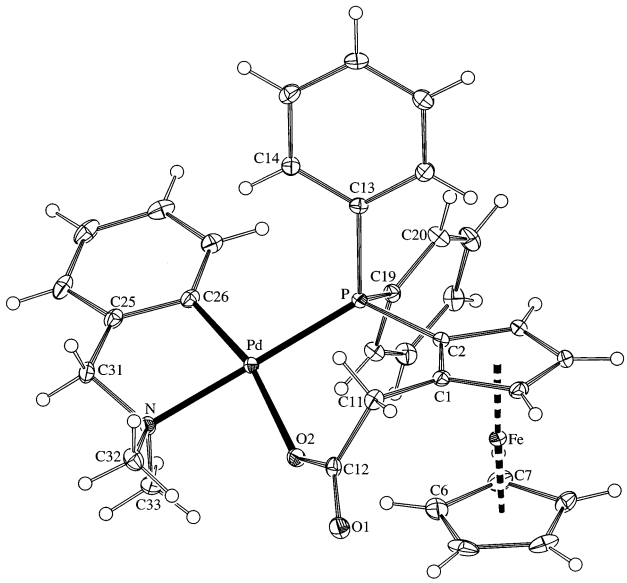


Figure 3. View of the molecular structure of complex **8** with the atom-labeling scheme. Thermal ellipsoids correspond to the 30% probability level.

are very similar to those reported for the analogous complex [$Pd(C_6H_4CH_2NMe_2$-κ^2C^1,N)($PhP_2CH_2CO_2$-κ^2O,

Table 2. Selected Geometric Parameters for 8[a]

Pd−P	2.2559(4)	C(26)−Pd-P	95.46(5)
Pd−O(2)	2.090(1)	P−Pd−O(2)	97.65(3)
Pd−N	2.145(2)	O(2)−Pd−N	83.78(5)
Pd−C(26)	2.017(2)	N−Pd−C(26)	83.00(6)
N−C[b]	1.476(2)−1.481(2)	Pd−O(2)−C(12)	135.1(1)
		C(11)−C(12)−O(2)	117.4(1)
		C(11)−C(1)−C(2)−P	6.5(3)
C(1)−C(11)	1.505(2)	C(2)−C(1)−C(11)	126.7(2)
C(11)−C(12)	1.525(2)	C(1)−C(11)-C(12)	112.0(1)
C(12)−O(1)	1.233(2)	O(1)−C(12)−O(2)	123.6(2)
C(12)−O(2)	1.285(2)	C(1)−C(2)−P	125.8(1)
P−C[c]	1.804(2)−1.833(2)	C−P−C[d]	101.31(8)−106.99(8)
Fe−Cg1	1.6560(8)	Cp1,Cp2	4.4(1)
Fe−Cg2	1.6591(9)	Cp1,Ph3	19.4(1)

[a] Distances are given in Å and angles in deg. Plane definitions (plane, defining atoms [ring centroid]): Cp1, C(1−5) [Cg(1)]; Cp2, C(6−10), [Cg(2)]; Ph1, C(13−18), [Cg(3)]; Ph2, C(19−24), [Cg(4)]; Ph3, C(25−30), [Cg(5)]. [b] The range of N−C(31,32,33) distances. [c] The range of P−(C2,13,19) distances. [d] The range of C(2)−P−C(13,19) and C(13)−P−C(19) angles.

P)],[2f] but the associated angles differ, since the presence of a larger chelate ring in **8** results in opening of the P−Pd−O angle. The Pd−P and Pd−O bond lengths compare very well to those of *cis*-[Pd($Ph_2PCH_2CO_2$-κ^2O,P)$_2$] (average values 2.235 and 2.076 Å, respectively),[27] whereas the Pd−P bond is significantly shorter than that in complexes with monodentate phosphinocarboxylic ligands, *trans*-[$PdBr_2(Ph_2PCH_2CO_2H$-$\kappa P)_2$] (2.322(2) Å)[28] and *trans*-[$PdCl_2$(Hdpf-κP)L_2]·2AcOH (2.363(1) Å).[16b] This corresponds to a higher trans influence of the halide and hydrocarbyl ligands, respectively, compared to O-bonded carboxylate.[29]

According to the ring puckering parameters[30] (Q_2 = 0.333(2) Å, ϕ_2 = 49.1(3)°), the conformation of the five-membered palladacycle is nearly halfway between envelope (ϕ_2 = 36°) and chair (ϕ_2 = 54°). Consequently, the aryl and coordination (PdL_4) planes deviate by 14.68(7)° from a coplanar arrangement. The other, seven-membered ring, which is oriented so that the phosphorus and nitrogen atoms are mutually trans, can be considered consisting of two parts: a nearly planar, four-membered {PC(2)C(1)C(11)} unit (maximum distance from the least-squares plane: 0.028(2) Å for C(1)), and a twisted link formed by the remaining three atoms {PdO(2)C(12)} that are all displaced from the plane of the four atoms in the same direction (perpendicular distances from the plane (Å): Pd, 1.087(1); C(12), 1.419(2); O(2), 1.899(2)).

Deprotonation and coordination affects the molecule of the carboxyphosphine only marginally. In comparison to Hpfa, the C−O distance is somewhat shortened while the C═O distance is very slightly elongated, both distances being similar to those in a complex with a chelating dpf$^-$ anion, *trans*-[Rh(CO)(PCy_3)(dpf-κ^2O,P)].[16c] The carboxyl group is rotated from the position observed in *rac*-Hpfa so as to conform to the steric demands of the palladium center (dihedral angle C(12)O(1)O(2) vs Cp1 64.6(2)°), though without any significant torsion at the C(1)−C(2) bond, the angle subtended by the carboxyl and PdL_4 planes being 43.3(2)°. As a result of coordination to palladium, the C−P−C angles in **8** are more opened than in *rac*-Hpfa, approaching the values for **5** and **6**.

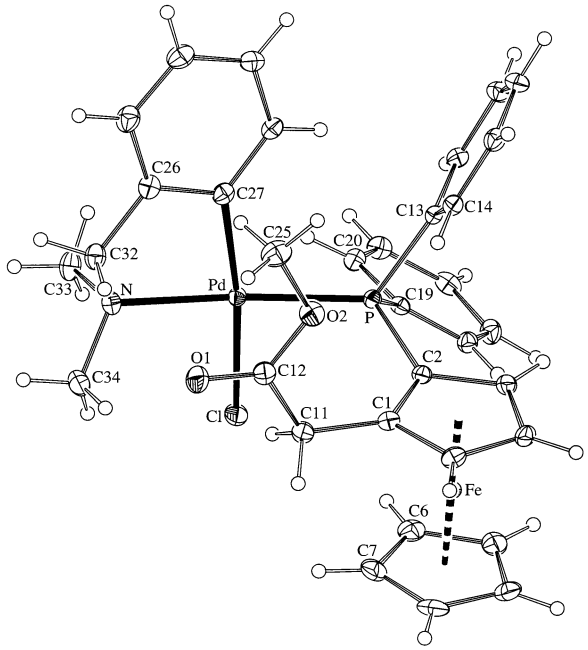


Figure 4. View of the molecular structure of complex **9** showing the atom-labeling scheme. Thermal ellipsoids are drawn at the 30% probability level.

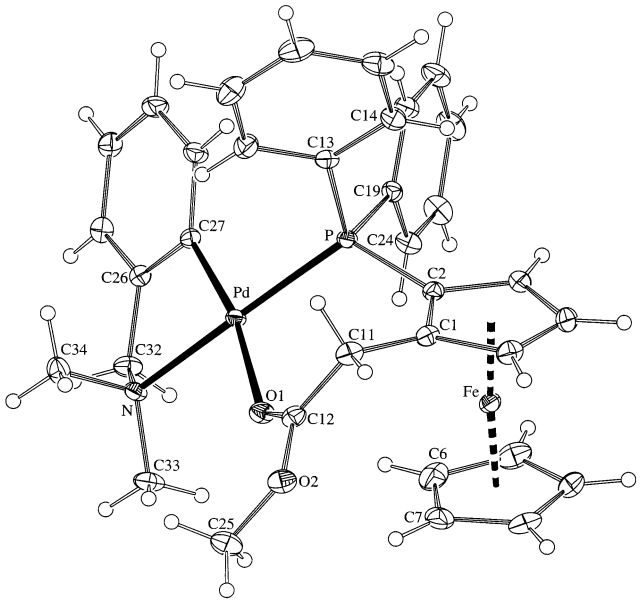


Figure 5. View of the molecular structure of complex **10** with the atom-labeling scheme. The perchlorate counterion has been omitted for clarity (see the Supporting Information and ref 31). Thermal ellipsoids are drawn at the 30% probability level.

Crystal Structures of 9 and 10. The structures of complexes **9** and **10** are shown in Figures 4 and 5, respectively, and the selected geometric parameters are given in Table 3. The structures are molecular, showing in the solid state only weak C−H···O (to ester or perchlorate oxygen atoms) and C−H···π-ring interac-

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(28) Polahová, J.; Loub, J.; Ječný, J. *Acta Crystallogr.* **1979**, *B35*, 328.
(29) Hartley, F. R. *The Chemistry of Platinum and Palladium*; Applied Science: London, 1973; pp 299−303.
(30) Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354. The ring puckering parameters should be interpreted with care because of unlike bond lengths within the metallacycle.

Table 3. Selected Geometric Data for 9 and 10[a]

param	**9** (X = Cl)[b]	**10** (X = O(1))[c]
Pd-X	2.3999(7)	2.152(1)
Pd−P	2.2790(7)	2.2416(4)
Pd−N	2.151(2)	2.145(1)
Pd−C(27)	2.013(3)	1.987(2)
N−C[d]	1.478(4)−1.495(3)	1.480(2)−1.489(2)
C(1)−C(11)	1.492(4)	1.505(2)
C(11)−C(12)	1.504(4)	1.497(2)
C(12)−O(1)	1.210(3)	1.225(2)
C(12)−O(2)	1.338(3)	1.324(2)
O(2)−C(25)	1.449(3)	1.453(2)
P−C[e]	1.814(2)−1.844(2)	1.798(2)−1.822(2)
Fe−Cg1	1.641(1)	1.6467(8)
Fe−Cg2	1.654(1)	1.655(1)
P−Pd−X	86.67(2)	97.78(3)
X−Pd−N	91.89(6)	88.67(5)
N−Pd−C(27)	81.77(9)	81.99(6)
C(27)−Pd−P	100.11(6)	92.12(5)
C(2)−C(1)−C(11)	128.8(2)	126.6(1)
C(1)−C(11)−C(12)	118.2(2)	114.4(1)
O(1)−C(12)−O(2)	123.3(2)	121.0(2)
C(12)−O(2)−C(25)	115.8(2)	115.7(1)
C−P−C[f]	98.5(1)−110.9(1)	100.41(7)−108.74(7)
C(1)−C(2)−P	127.4(2)	123.3(1)
C(11)−C(1)−C(2)−P	15.9(4)	−6.7(2)
Cp1,Cp2	3.2(2)	4.8(1)
Cp1,CO(1)O(2)	84.3(3)	55.1(2)
Cp1,Ph3	75.8(1)	69.47(9)
PdL_4,Ph3	19.0(1)	26.95(6)
PdL_4,CO(1)O(2)	12.8(3)	22.2(2)
Q_2, ϕ_2[g]	0.385(2), 36.9(4)	0.443(1), 210.9(2)

[a] Distances are given in Å and angles in deg. Plane definitions (plane, defining atoms [ring centroid]): Cp1, C(1−5) [Cg(1)]; Cp2, C(6−10), [Cg(2)]; Ph1, C(13−18), [Cg(3)]; Ph2, C(19−24), [Cg(4)]; Ph3, C(26−31), [Cg(5)]; PdL_4, {Pd,X,P,N, C(27)}. [b] **9**: Pd···C(11) = 3.365(3) Å, Pd···C(12) = 3.387(3) Å, Pd···O(1) = 3.831(2) Å, Pd···O(2) = 3.664(2) Å. [c] **10**: Pd−O(1)−C(12) = 136.5(1)°, C(11)−C(12)−O(1) = 126.4(2)°. [d] N−C(32,33,34) distances. [e] P−(2,12,19) distances. [f] C(2)−P−C(13,19) and C(13)−P−C(19) angles. [g] The ring puckering parameters.

tions.[31] In both cases the coordination environments around the palladium centers are very nearly planar and, as indicated by the sum of angles around the palladium atom (**9**, 360.4°; **10**, 360.6°) and deviations from the least-squares planes defined by the central atom and the four donor atoms (PdL_4), only slightly more distorted than that in **8**. The orientations of the palladated aryl ring toward the PdL_4 plane in **8**−**10** are similar, though with a deviation from a coplanar arrangement increasing in the same order: **8** < **9** < **10**. The five-membered palladacycles in **9** and **10** adopt different conformations: a perfect envelope in **9** and an intermediate conformation between an ideal envelope and a half-chair in **10**. The Pd−donor bond lengths in **9** are only very slightly shorter than distances in **8** or in an analogous complex, [*SP*-4-4]-bromo{2-[(dimethylamino-κN)methyl]phenyl-κC^1}{ethyl (diphenylphosphino)-acetate-κP}palladium(II),[26d] and the geometry of the carboxyl group is quite comparable to that in uncoordinated Hpfa. Surprisingly, the uncoordinated ester function does not act in the solid state as an innocent spectator group but, instead, the CH_2CO_2Me pendant arm is rotated above the palladium center so that the carbonyl carbon atom C(12) is placed just above the palladium atom at a distance of 3.387(3) Å (cf. the perpendicular distance of palladium atom from the carboxyl C(12)O(1)O(2) plane of 3.264(6) Å). Other Pd···O,C distances (Table 3) point to a rather unusual side-on interaction between palladium and C(12) atoms rather than to an interaction with σ- and π-electron density of the C−O and C═O bonds, respectively.[32] This weak interaction, not revealed in IR spectra, most likely accounts for a notable torsion at the C(1)−C(2) bond (torsion angle 15.9(4)°).

The conversion of **9** into **10** brings about no dramatic change of the individual geometric parameters; subtle relative variations in the palladium−donor distances common to **9** and **10** can be explained in terms of an increased donation to the electron poor central atom, which results in a slight shortening of the Pd−donor bond lengths (Table 3; the maximum relative shortening of about 2% is observed for the Pd−P bond length and the Pd−N and Pd−C distances are shortened by ca. 0.3% and 1%, respectively). Due to an induced electron density shift from Ph to phosphorus, this effect is, to a comparable extent, relayed further to P−C bonds. A replacement of chloride ligand in **9** with carbonyl oxygen results in opening of the P−Pd−X bond angle, where X = Cl (**9**), O(1) (**10**), by about 11°. This change reflects the steric properties of the O,P-chelate ligand and is compensated by closing of the X−Pd−N and C−Pd−P (but not N−Pd−C) angles. Furthermore, the coordination of the carbonyl oxygen results in a slight elongation of the C═O bond and a very similar shortening of the C−O bond. Hence, the electron density lowering at O(1) and the carbonyl carbon atom C(12) appears to be compensated by an electron density transfer from O(2), though not fully, as indicated by a low-field shift of the carbonyl resonance in the ^{13}C NMR spectra. Notably, the chelate formation releases torsional strain at the C(1)−C(2) bond, as observed in **9**. The internal geometry of the CH_2COO pendant arm remains unchanged (cf. bond lengths and angles for Hpfa and **9**), but the carboxyl plane has a different orientation toward the PdL_4 and Cp1 planes (see Table 3 for definitions). In comparison to **8**, which has a similar seven-membered chelate ring, the angles subtended by the carboxyl group {C(12)O(1)O(2)} and the PdL_4 and Cp1 planes in **10** are more acute.

Discussion and Conclusions

Considering the previous report that **1** reacts with MeI to give either mono- or dialkylated products de-

(31) Although weak, the C−H···O interactions in the structure of **10** seem to fix the position of the perchlorate counterion and thus prevent this symmetrical species from disorder, which is frequently encountered among perchlorate salts. The most prominent C···O contacts in **10** are as follows: C(5)−H(5)···O(12)$^{\&(x,3/2-y,1/2+z)}$, 3.177(3) Å; C(34)−H(34C)···O(12)$^{\&(x,y-1,z)}$, 3.330(3) Å; C(35)−H(25C)···O(11)$^{\&(-x,y-1/2,1/2-z)}$, 3.344(3) Å. For a detailed list of the metric parameters (**9** and **10**) and a diagram showing the C−H···O contacts in the structure of **10**, see the Supporting Information.

(32) A search for similar systems featuring palladium atom and an O···C···O moiety (··· stands for an unspecified bond) in the Cambridge Structural Database revealed only several compounds with intermolecular Pd···C distances in the range 2.7−4.5 Å. Most of the Pd···C contacts, however, were longer and appeared rather incidental, due to an unfavorable orientation of the carboxyl plane. An example of a suitably orientated but more distant carboxyl plane is a complex with an oxazolinyl-modified acetylglucopyranoside (Pd···C = 3.85 Å): (a) Boog-Wick, K.; Pregosin, P. S.; Worle, M.; Albinati, A. *Helv. Chim. Acta* **1998**, *81*, 1622. On the other hand, the shortest contact (2.85 Å) but an unfavorable arrangement (offset position) was found in a palladium(II) complex with a methoxycarbonyl-substituted hydrocarbyl ligand: (b) Goddard, R.; Green, M.; Hughes, R. P.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1976**, 1890. A possible interaction was not mentioned in either case.

pending on the amount of the alkylating agent while a compound analogous to **1** bearing an additional CPh_2(OH) group at the other position adjacent to the aminomethyl group is only monoalkylated with MeI,[12a] it is likely that the course of the alkylation reaction is controlled by spatial arrangement of the primary (N-alkylated) product and steric demands of the alkylating agent. The use of benzyl bromide[33] as a more bulky yet powerful alkylating agent in alkylation of **1** is advantageous due to the alkylation reaction proceeding fast and cleanly to give the well-defined, air-stable monoalkylated product **2**. Ammonium salt **2** can be converted without isolation by a standard procedure[34] to nitrile **3** which, after basic hydrolysis, affords the phosphinocarboxylic acid Hpfa (in 63% overall yield based on **1**). The acid was further converted to the corresponding phosphine oxide and sulfide and to the methyl ester **4**. The structures of compounds **2**, **3**, *rac*-Hpfa, **5**, and **6** were determined by single-crystal X-ray diffraction. In the structures of noncoordinated acids Hpfa, **5**, and **6**, the carboxyl groups are involved in hydrogen bonding to either neighboring carboxyl groups or the phosphinoyl moiety, forming closed supramolecular assemblies.

Testing *rac*-Hpfa and **4** as ligands in palladium(II) complexes revealed the compounds to easily form heterobimetallic complexes with the P-coordinated ester **4** (Hpfa analogues are unstable, see above) or O,P-chelating neutral **4** and anionic pfa^- donors. The respective complexes **8**−**10** were characterized by X-ray crystallography. A comparison of their *solid-state* structures with the structures of Hpfa and its simple derivatives (**3**, **5**, and **6**) indicates the studied ferrocene ligands to behave as a rather rigid phosphinoferrocene ligands modified by an attached flexible carboxymethylene side arm: whereas the phosphino part changes its arrangement only upon introduction of a "fourth" substituent (oxidation to P^V or coordination), the carboxymethylene pendant group easily undergoes conformational changes to form stable O,P-chelates (**8** and **10**) or phosphine-like complexes with an "uncoordinated" polar group weakly interacting with the central atom in a nonclassical manner (**9**). Ligand bite angles O−Pd−P in complexes with chelating pfa^- (**8**, 97.65(3)°) and **4** (**10**, 97.78(3)°) are practically identical, indicating similar steric properties of the chelate ligands. In all the cases, the Pd···Fe distances exceed the sum of van der Waals radii (**8**, 4.5691(3) Å; **9**, 4.8988(4) Å; **10**, 4.4274(2) Å).

In conclusion, *rac*-Hpfa represents a new entry among ferrocene phosphinocarboxylic acids (see Chart 1), other functionalized ferrocenecarboxylic acids,[35] and the related compounds mentioned above. *rac*-Hpfa and **4** can be considered as a pair of complementary hybrid ligands capable of further interactions with proximal polar groups. Further studies on the coordination behavior of *rac*-Hpfa and its derivatives as well as the preparation of enantiopure Hpfa aimed at an application of these compounds as ligands in catalysis are currently under way.

Experimental Section

General Comments. Unless specified otherwise, all syntheses were carried under an argon blanket with exclusion of direct daylight. Acetonitrile was dried by standing over phosphorus pentoxide and then distilled and stored over 4 Å molecular sieves. Toluene and dichloromethane were dried with potassium metal and potassium carbonate, respectively, and distilled. Diethyl ether and hexane for crystallizations were used without purification. *rac*-*N*,*N*-Dimethyl[2-(diphenylphosphino)ferrocenyl]methylamine (**1**)[12a] and di-μ-chlorobis{2-[(dimethylamino)methyl-κN)phenyl-κC^1}dipalladium(II) (**7**)[36] were synthesized by the literature procedures. All other chemicals were used as received from commercial suppliers.

NMR spectra were recorded on a Varian UNITY Inova 400 spectrometer (^{1}H, 399.95 MHz; ^{13}C, 100.58 MHz; ^{31}P, 161.90 MHz) at 298 K. Chemical shifts (δ/ppm) are given relative to an internal tetramethylsilane (^{1}H and ^{13}C) or external 85% aqueous H_3PO_4 (^{31}P). The assignment of NMR signals is based on 1D and 2D (COSY, relayed-COSY, gHSQC, and gHMBC) NMR experiments. IR spectra were recorded on an FT IR Nicolet Magna 650 instrument in the range of 400−4000 cm^{-1}. Melting points were determined on a Kofler apparatus and are uncorrected.

Safety Note. *Caution!* Perchlorate salts of cationic transition-metal complexes are potentially explosive. Only small amounts of such compounds should be prepared, and they should be handled with care.

Preparation of *rac*-[2-(diphenylphosphino)ferrocenyl]-acetonitrile (3). A a solution of benzyl bromide (1.80 g, 10.5 mmol) in dry acetonitrile (5 mL) was added dropwise into a suspension of *rac*-**1** (4.274 g, 10.0 mmol) in the same solvent (100 mL) at room temperature. The solid amine dissolved quickly to give a clear orange solution. After the mixture was stirred for 1 h, the volatiles were removed under reduced pressure at a temperature not exceeding 35 °C, and the resulting orange foam was immediately mixed with a solution of sodium cyanide (4.90 g, 0.10 mol) in water (100 mL). The heterogeneous reaction mixture was refluxed in air for 8 h with vigorous stirring and then cooled to room temperature, whereupon the crude product, originally a dark oil, solidified to a dark solid mass. The aqueous phase was separated and extracted with diethyl ether. The solid material was dissolved in diethyl ether. The etheral solutions were combined, washed well with water, dried over magnesium sulfate, and passed through a short silica gel column (elution with ether) to remove polar impurities. The eluate was evaporated under reduced pressure and the residue crystallized from hot aqueous acetic acid to give **3** as an orange crystalline solid (2.935 g, 72%). GC-MS analysis of the crude etheral extract revealed the presence of *N*,*N*-dimethylbenzylamine.

Mp: 133−135 °C. ^{1}H NMR ($CDCl_3$): δ 3.23 (dd, $^2J_{HH}$ = 18.3, $^4J_{PH}$ = 1.2 Hz, 1 H, CH_2), 3.74 (d, $^2J_{HH}$ = 18.3 Hz, 1 H, CH_2), 3.77 (m, 1 H, C_5H_3), 4.14 (s, 5 H, C_5H_5), 4.33 (apparent t, *J*. 2.5 Hz, 1 H, C_5H_3), 4.63 (dt, *J*. 2.5, 1.6 Hz, 1 H, C_5H_3), 7.08−7.54 (m, 10 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 17.83 (d, $^3J_{PC}$ = 13 Hz, *C*H_2), 69.47 (*C*H C_5H_3), 70.26 (C_5H_5), 70.70 (d, J_{PC} = 3 Hz, *C*H C_5H_3), 71.60 (d, J_{PC} = 3 Hz, *C*H C_5H_3), 75.90 (d, $^1J_{PC}$ = 8 Hz, *C*-P C_5H_3), 85.17 (d, $^2J_{PC}$ = 25 Hz, *C*-CH_2 C_5H_3), 117.90 (*C*≡N), 128.33 (d, $^3J_{PC}$ = 8 Hz, *C*H$_m$ PPh_2), 128.35 (d, $^3J_{PC}$ = 6 Hz, *C*H$_m$ PPh_2), 128.44 (*C*H$_p$ PPh_2), 129.41 (d, $^4J_{PC}$. 1 Hz, *C*H$_p$ PPh_2), 132.15 (d, $^2J_{PC}$ = 18 Hz, *C*H$_o$ PPh_2), 134.77 (d, $^2J_{PC}$ = 21 Hz, *C*H$_o$ PPh_2), 136.21 (d, $^1J_{PC}$ = 8 Hz, C_{ipso} PPh_2), 138.52 (d, $^1J_{PC}$ = 10 Hz, C_{ipso} PPh_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −23.6 (s). IR (Nujol; $\tilde{\nu}$/cm^{-1}) $\nu_{C\equiv N}$ 2251 w; 1304 w, 1240 w, 1168

(33) Benzyl chloride and iodide have already been used in alkylation of $FcCH_2NMe$ and the salts used in the synthesis of (ferrocenyl)methyl derivatives. For references see: (a) Perevalova, E. G.; Ustynyuk, Yu. A.; Nesmeyanov, A. N. *Izv. Akad. Nauk SSSR* **1963**, 1036. (b) Nesmeyanov, A. N.; Perevalova, E. G.; Leonteva, L. I.; Ustynyuk, Yu. A. *Izv. Akad. Nauk SSSR* **1965**, 1696.

(34) Lednicer, D.; Lindsay, J. K.; Hauser, C. R. *J. Org. Chem.* **1958**, *23*, 653.

(35) For instance, 2-[1-(dimethylamino)ethyl]- and 2-(1-hydroxyethyl)ferrocenecarboxylic acids (the latter only in the form of esters): Cullen, W. R.; Wickenheiser, E. B. *Can. J. Chem.* **1990**, *68*, 705.

(36) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909.

w, 1166 m, 1105 m, 1068 m, 1035 m, 1023 m, 997 m, 828 s, 814 m, 748 vs, 697 s, 551 m, 494 s, 486 vs, 457 vs. Anal. Calcd for $C_{24}H_{20}FeNP$: C, 70.44; H, 4.93; N, 3.42. Found: C, 70.27; H, 5.06; N, 3.36.

In Situ NMR Study of the Alkylation Reaction. A solution of benzyl bromide (16.8 mg, 0.98 mmol) in acetonitrile-d_3 (0.70 mL) was added to a suspension of *rac*-**1** (42.5 mg, 0.99 mmol) in the same solvent (0.7 mL). The mixture was stirred at room temperature until all the amine dissolved, and the solution was transferred into an NMR tube and analyzed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. The spectra recorded 30 min, 60 min, and 24 h after mixing the reagents were identical.

Addition of another 1 equiv of $PhCH_2Br$ to the reaction mixture caused a rapid separation of well-developed rusty orange microcrystals. Therefore, the dialkylation was attempted in a separate flask by mixing solutions of *rac*-**1** (42.8 mg, 0.1 mmol) and benzyl bromide (35.2 mg, 0.21 mmol) in anhydrous acetonitrile (0.7 and 0.5 mL, respectively). Shortly after mixing, a separation of orange microcrystals started. After the mixture stood for 30 min at room temperature and then at 0 °C overnight, the precipitate was filtered off, washed with diethyl ether, and dried in air. ^{1}H and ^{31}P{^{1}H} NMR spectra in DMSO-d_6 have shown the solid to be pure **2**. Yield: 46.8 mg (78%), rusty orange crystalline solid.

Data for **1** are as follows. NMR (CD_3CN): δ_H 1.97 (s, 6 H, N*Me*$_2$), 3.15 (d, $^2J_{HH}$ = 12.7 Hz, 1 H, CH_2), 3.73 (dd, $^2J_{HH}$ = 12.7, $^4J_{PH}$ = 2.6 Hz, 1 H, CH_2), 3.88 (m, 1 H, C_5H_3), 3.92 (s, 5 H, C_5H_5), 4.34 (apparent t, 1 H, C_5H_3), 4.50 (m, 1 H, C_5H_3), 7.12−7.66 (m, 10 H, P*Ph*$_2$); δ_P −22.8 (s). NMR (DMSO-d_6): δ_H 1.92 (s, 6 H, N*Me*$_2$), 3.19 (d, $^2J_{HH}$ = 12.7 Hz, 1 H, CH_2), 3.61 (dd, $^2J_{HH}$ = 12.7, $^4J_{PH}$ = 2.7 Hz, 1 H, CH_2), 3.83 (m, 1 H, C_5H_3), 3.91 (s, 5 H, C_5H_5), 4.36 (apparent t, 1 H, C_5H_3), 4.51 (m, 1 H, C_5H_3), 7.07−7.62 (m, 10 H, P*Ph*$_2$); δ_P −23.8 (s).

Data for *rac*-benzyldimethyl{2-[(diphenylphosphino)ferrocenyl]methyl}ammonium bromide (**2**) are as follows. NMR (CD_3CN): δ_H 2.51, 2.85 (2H s, 3 H, N*Me*$_2$), 4.03 (s, 5 H, C_5H_5), 4.36 (m, 1 H, C_5H_3), 4.40, 4.44 (2H d, $^2J_{HH}$ = 12.7 Hz, 1 H, AB PhCH_2), ca. 4.74 (apparent t, 1 H, C_5H_3), ca. 4.75 (dd, $^2J_{HH}$ = 13.4, J = 4.1 Hz, 1 H, $C_5H_3CH_2$), 5.03 (dt, J = 1.3, 2.4 Hz, 1 H, C_5H_3), 5.18 (d, $^2J_{HH}$ = 13.4 Hz, 1 H, $C_5H_3CH_2$), 7.20−7.69 (m, 15 H, *Ph*); δ_P −27.4 (s). NMR (DMSO-d_6): δ_H 2.46, 2.80 (2H s, 3 H, N*Me*$_2$); 3.99 (s, 5 H, C_5H_5), 4.35 (m, 1 H, C_5H_3), 4.35, 4.41 (2H d, $^2J_{HH}$ = 12.5 Hz, 1 H, AB PhCH_2); 4.71 (dd, $^2J_{HH}$ = 13.4, J = 3.8 Hz, 1 H, $C_5H_3CH_2$), 4.79 (apparent t, 1 H, C_5H_3), 4.88 (d, $^2J_{HH}$ = 13.4 Hz, 1 H, $C_5H_3CH_2$), 5.05 (m, 1 H, C_5H_3), 7.17−7.69 (m, 15 H, *Ph*); δ_P −27.9 (s). Anal. Calcd for $C_{32}H_{33}BrFePN$: C, 64.24; H, 5.56; N, 2.34. Found: C, 63.92; H, 5.45; N, 2.60.

Preparation of *rac*-[2-(Diphenylphosphino)ferrocenyl]acetic Acid, *rac*-Hpfa. A solution of KOH (5.07 g, 90 mmol) in water (50 mL) was added to a suspension of nitrile **3** (1.229 g, 3.0 mmol) in ethanol (50 mL), and the resulting heterogeneous mixture was refluxed for 24 h in air. During this period the nitrile dissolved to give a clear orange solution. After it was cooled to room temperature, the mixture was acidified by addition of 20% aqueous H_2SO_4 to precipitate crude Hpfa as a yellow flaky solid. Ethanol was then removed under reduced pressure, and the crude product was filtered off and washed with water. Subsequent recrystallization from hot aqueous acetic acid and drying under vacuum afforded pure *rac*-Hpfa as a yellow-orange flaky solid (1.128 g, 88%).

Mp: ca. 166−169 °C dec. ^{1}H NMR ($CDCl_3$): δ 3.55 (br d with weak AB sattelites, 2 H, CH_2), 3.77 (m, 1 H, C_5H_3), 4.01 (s, 5 H, C_5H_5), 4.30 (apparent t, $J \approx$ 2.5 Hz, 1 H, C_5H_3), 4.54 (m, 1 H, C_5H_3), 7.11−7.59 (m, 10 H, P*Ph*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 33.96 (d, $^3J_{PC}$ = 11 Hz, *C*H$_2$), 69.62 (*C*H C_5H_3), 69.88 (C_5H_5), 71.19 (d, J_{PC} = 3 Hz, *C*H C_5H_3), 71.85 (d, J_{PC} = 4 Hz, *C*H C_5H_3), 76.12 (d, $^1J_{PC}$ = 6 Hz, *C*-P C_5H_3), 85.39 (d, $^2J_{PC}$ = 26 Hz, *C*-CH$_2$ C_5H_3), 127.97 (d, $^3J_{PC}$ = 7 Hz, *C*H$_m$ PPh$_2$), 128.10 (d, $^3J_{PC}$ = 8 Hz, *C*H$_m$ PPh$_2$), 128.21, 128.91 (2H *C*H$_p$ PPh$_2$), 132.32 (d, $^2J_{PC}$ = 18 Hz, *C*H$_o$ PPh$_2$), 134.95 (d, $^2J_{PC}$ = 21 Hz, *C*H$_o$ PPh$_2$), 137.03 (d, $^1J_{PC}$ = 7 Hz, C_{ipso} PPh$_2$), 139.02 (d, $^1J_{PC}$ = 9 Hz, C_{ipso} PPh$_2$), 176.24 (*C*O$_2$H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −22.5 (s). IR (Nujol; $\tilde{\nu}$/cm^{-1}) $\nu_{C=O}$ 1712 vs, 1695 sh; 1251 m, 1217 s, 1154 m, 1106 m, 1069 m composite, 1003 m, 960 br m, 824 s, 751 vs, 741 vs, 699 vs, 498 s, 487 s, 456 m. Anal. Calcd for $C_{24}H_{21}FeO_2P$: C, 67.31; H, 4.94. Found: C, 67.50; H, 4.89.

Preparation of *rac*-Methyl [2-(Diphenylphosphino)-ferrocenyl]acetate (4). In air, solid *rac*-Hpfa (214.2 mg, 0.50 mmol) was added to a solution of diazomethane (ca. 5 equiv) in diethyl ether (20 mL). The solid dissolved with vigorous effervescence to a clear solution. After standing for 30 min at room temperature, the solution was evaporated, the residue was dissolved in dichloromethanee, and this mixture was purified by flash chromatography on silica gel (elution with dichloromethane). Evaporation of the eluate and drying in vacuo gave **4** as an orange solid (204.2 mg, 92%).

^{1}H NMR ($CDCl_3$): δ 3.33 (s, 3 H, O*Me*), 3.49 (d, $^2J_{HH}$ = 15.7 Hz, 1 H, CH_2), 3.62 (dd, $^2J_{HH}$ = 15.7, $^4J_{PH}$ = 2.4 Hz, 1 H, CH_2), 3.76 (m, 1 H, C_5H_3), 4.01 (s, 5 H, C_5H_5), 4.30 (apparent t, 1 H, C_5H_3), 4.55 (m, 1 H, C_5H_3), 7.13−7.58 (m, 10 H, P*Ph*$_2$). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 34.40 (d, $^3J_{PC}$ = 10 Hz, *C*H$_2$), 51.39 (O*Me*), 69.55 (*C*H C_5H_3), 69.79 (C_5H_5), 71.20 (d, J_{PC} = 4 Hz, *C*H C_5H_3), 72.00 (d, J_{PC} = 4 Hz, *C*H C_5H_3), 76.06 (d, $^1J_{PC}$ = 7 Hz, *C*-P C_5H_3), 856.24 (d, $^2J_{PC}$ = 26 Hz, *C*-CH$_2$ C_5H_3), 127.82 (*C*H$_p$ PPh$_2$), 127.99 (d, $^3J_{PC}$ = 6 Hz, *C*H$_m$ PPh$_2$), 128.13 (d, $^3J_{PC}$ = 8 Hz, *C*H$_m$ PPh$_2$), 129.14 (*C*H$_p$ PPh$_2$), 132.37 (d, $^2J_{PC}$ = 18 Hz, *C*H$_o$ PPh$_2$), 134.95 (d, $^2J_{PC}$ = 21 Hz, *C*H$_o$ PPh$_2$), 137.17 (d, $^1J_{PC}$ = 7 Hz, C_{ipso} PPh$_2$), 139.31 (d, $^1J_{PC}$ = 9 Hz, C_{ipso} PPh$_2$), 171.27 (*C*O$_2$H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −22.9 (s). IR (Nujol; $\tilde{\nu}$/cm^{-1}): $\nu_{C=O}$ 1734 vs; 1584 m, 1308 s, 1261 s, 1236 m, 1173 s, 1130 m, 1104 s, 1020 m, 1005 s, 999 s, 845 m, 835 m, 814 s, 749 vs, 744 vs, 701 vs, 496 vs, 488 s, 453 s, 441 s. Anal. Calcd for $C_{25}H_{23}FeO_2P$: C, 67.89; H, 5.24. Found: C, 67.80; H, 5.25.

Preparation of *rac*-[2-(Diphenylphosphinoyl)ferrocenyl]acetic Acid (5). In air, a solution of Hpfa (107 mg, 0.25 mmol) in acetone (10 mL) was cooled in an ice bath and treated with excess aqueous hydrogen peroxide (0.5 mL 30%) with stirring. After it was stirred for another 30 min at 0 °C, the mixture was diluted with water and acetone was removed under reduced pressure. The precipitated solid was filtered off, washed with water, and dried under vacuum. The solid was dissolved in methanol and the solution filtered and evaporated. The residue was dried under vacuum to furnish **5** as an ochre solid in virtually quantitative yield.

^{1}H NMR ($CDCl_3$): δ 3.29, 3.37 (2H d, $^2J_{HH}$ = 13.5 Hz, 1 H, CH_2), 3.99 (apparent q, J = 1.3 Hz, 1 H, C_5H_3), 4.13 (s, 5 H, C_5H_5), 4.46 (apparent q, J = 2.4 Hz, 1 H, C_5H_3), 4.63 (br apparent q, 1 H, C_5H_3), 7.36−7.86 (m, 10 H, P*Ph*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 35.17 (*C*H$_2$), 68.76 (d, $^1J_{PC}$ = 115 Hz, *C*-P C_5H_3), 70.76 (d, J_{PC} = 12 Hz, *C*H C_5H_3), 71.22 (C_5H_5), 71.88 (d, J_{PC} = 15 Hz, *C*H C_5H_3), 75.40 (d, J_{PC} = 10 Hz, *C*H C_5H_3), 128.54, 128.74 (2H d, $^3J_{PC}$ = 12 Hz, *C*H$_m$ PPh$_2$), 131.08 (d, $^1J_{PC}$ = 110 Hz, C_{ipso} PPh$_2$), 131.34, 131.39 (2H d, $^2J_{PC}$ = 10 Hz, *C*H$_o$ PPh$_2$), 132.62 (d, $^1J_{PC}$ = 108 Hz, C_{ipso} PPh$_2$), 132.44 (d, $^4J_{PC}$ = 3 Hz, *C*H$_p$ PPh$_2$), 132.55 (d, $^4J_{PC}$ = 2 Hz, *C*H$_p$ PPh$_2$), 170.79 (*C*O$_2$H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ +37.1 (s). Anal. Calcd for $C_{24}H_{21}FeO_3P$: C, 64.89; H, 4.76. Found: C, 64.57; H, 4.91.

Preparation of *rac*-[2-(Diphenylthiophosphoryl)ferrocenyl]acetic Acid (6). A mixture of *rac*-Hpfa (107 mg, 0.25 mmol), sulfur (16 mg, 0.50 mmol) and toluene (5 mL) was heated to 100 °C for 1 h, yielding first a clear yellow-orange solution which later deposited an orange precipitate. The mixture was cooled in an ice bath, and the precipitated phosphine sulfide was filtered off, washed with hexane, and dried in air. Yield: 105 mg, 91% (orange solid).

^{1}H NMR ($CDCl_3$): δ 3.71 (d, $^2J_{HH}$ = 16.5 Hz, 1 H, CH_2), 3.78 (m, 1 H, C_5H_3), 4.07 (d, $^2J_{HH}$ = 16.5 Hz, 1 H, CH_2), 4.30 (s, 5 H, C_5H_5), 4.35 (dt, $J \approx$ 1.6, 2.6 Hz, 1 H, C_5H_3), 4.62 (m, 1 H, C_5H_3), 7.32−7.86 (m, 10 H, P*Ph*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 33.62 (*C*H$_2$), 69.51 (d, J_{PC} = 10 Hz, *C*H C_5H_3), 71.08 (C_5H_5),

74.00 (d, $^1J_{PC}$ = 95 Hz, *C*-P C_5H_3), 74.18 (d, J_{PC} = 12 Hz, *C*H C_5H_3), 74.27 (d, J_{PC} = 9 Hz, *C*H C_5H_3), 84.35 (d, $^2J_{PC}$ = 12 Hz, *C*-CH_2 C_5H_3), 128.10 (d, $^3J_{PC}$ = 12 Hz, *C*H_m PPh_2), 128.27 (d, $^3J_{PC}$ = 13 Hz, *C*H_m PPh_2), 131.42, 131.47 (2H d, $^4J_{PC}$ = 3 Hz, *C*H_p PPh_2); 131.90 (d, $^2J_{PC}$ = 10 Hz, *C*H_o PPh_2), 132.09 (d, $^2J_{PC}$ = 11 Hz, *C*H_o PPh_2), 132.89, 134.11 (2H d, $^1J_{PC}$ = 87 Hz, C_{ipso} PPh_2); 174.05 (*C*O_2H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 42.3 (s). Anal. Calcd for $C_{24}H_{21}FeO_2PS$: C, 62.62; H, 4.60. Found: C, 62.17; H, 4.44.

Prepation of[*SP*-4−3]-{2-[(Dimethylamino-κN)methyl]-phenyl-κC^1}{*rac*-2-(diphenylphosphino-κP)ferrocenylacetato-κO^1}palladium(II) (8). Solid potassium *tert*-butoxide (24 mg, 0.21 mmol) was added to a solution of *rac*-Hpfa (90 mg, 0.21 mmol) in dichloromethane (10 mL), and the mixture was stirred at room temperature for 30 min. Formation of some precipitate was observed during this period. Then, the in situ generated carboxylate salt was treated with a solution of **7** (55 mg, 0.10 mmol) in dichloromethane (2 mL), whereupon the precipitate dissolved quickly to give a clear yellow-orange solution. After the mixture was stirred for another 1 day at room temperature, all volatiles were removed under reduced pressure, the residue was extracted with dichloromethane (2 × 2 mL) to remove KCl, and the extracts were filtered. Diethyl ether (10 mL) was carefully added as the top layer to the filtrate, and the mixture was allowed to crystallize for several days at room temperature to give **8** as well-developed rusty orange microcrystals which were isolated by suction and dried under vacuum. The mother liquor was evaporated and the residue crystallized as above to give a second crop of crystals. Combined yield: 117 mg, 88%.

^1H NMR ($CDCl_3$): δ 2.78 (d, $^4J_{PH}$ = 2.5 Hz, 3 H, N*Me*), 2.92 (d, $^2J_{HH}$ = 13.4 Hz, 1 H, CH_2CO_2), 2.97 (d, $^4J_{PH}$ = 2.9 Hz, 3 H, N*Me*), 3.10 (d, $^2J_{HH}$ = 13.4 Hz, 1 H, CH_2CO_2), 3.50 (m, 1 H, C_5H_3), 3.91 (dd, $^2J_{HH}$ = 13.8, $^4J_{PH}$ = 2.9 Hz, 1 H, CH_2N), 4.21 (at, 1 H, C_5H_3), 4.22 (br d, $^2J_{HH} \approx$ 13.8 Hz, 1 H, CH_2N), 4.28 (s, 5 H, C_5H_5), 4.50 (m, 1 H, C_5H_3), 6.31−7.87 (m, 14 H, aromatics). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 37.61 (*C*H_2CO_2), 49.30, 49.88 (2H d, $^3J_{PC}$ = 2 Hz, N*Me*, 68.07 (*C*H C_5H_3), 71.27 (C_5H_5), 71.89 (d, $^3J_{PC}$ = 3 Hz, N*C*H_2), 72.01 (d, $^1J_{PC}$ = 59 Hz, *C*-P C_5H_3), 72.35 (d, J_{PC} = 3 Hz, *C*H C_5H_3), 75.07 (d, J_{PC} = 9 Hz, *C*H C_5H_3), 88.37 (d, $^2J_{PC}$ = 16 Hz, *C*-CH_2 C_5H_3), 122.54, 124.09 (*C*H C_6H_4), 125.06 (d, J_{PC} = 5 Hz, *C*H C_6H_4), 128.08 (d, J_{PC} = 11 Hz, *C*H PPh_2), 125.58 (d, J_{PC} = 10 Hz, *C*H PPh_2), 129.91 (d, $^1J_{PC}$ = 46 Hz, *C*-P PPh_2), 130.50 (d, $^1J_{PC}$ = 55 Hz, *C*-P PPh_2), 130.92, 130.98 (2H d, J_{PC} = 2 Hz, *C*H PPh_2), 134.25 (d, J_{PC} = 12 Hz, *C*H PPh_2), 134.95 (d, J_{PC} = 13 Hz, *C*H PPh_2), 138.46 (d, J_{PC} = 12 Hz, *C*H C_6H_4), 144.23 (d, J_{PC} = 4 Hz, C_{ipso} C_6H_4), 148.88 (d, J_{PC} = 2 Hz, C_{ipso} C_6H_4), 175.72 (*C*O_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.5 (s). IR (Nujol; $\tilde{\nu}$/cm^{-1}) $\nu_{C=O}$ 1622 vs, 1592 vs, 1580 vs; 1173 m, 1107 m, 1098 m br; 999 m br; 975 m, 927 m br, 851 m, 826 w, 817 m, 737 s composite, 696 s, 638 w, 607 w, 541 m, 527 s, 504 s, 497 s, 480 m, 467 m, 452 m. Anal. Calcd for $C_{33}H_{32}FeNO_2PPd$: C, 59.35; H, 4.83; N, 2.10. Found: C, 59.28; H, 4.72; N, 2.03.

Preparation of [*SP*-4-4]-Chloro{2-[(dimethylamino-κN)methyl]phenyl-κC^1}{*rac*-methyl [2-(diphenylphosphino)ferrocenyl]acetate-κP}palladium(II) (9). A solution of **4** (93.4 mg, 0.21 mmol) in dichloromethane (1 mL) was added to a solution of the dimer **7** (55.2 mg, 0.10 mmol) in the same solvent (2 mL). After it stood for 90 min at room temperature, hexane was added as the top layer to the clear orange solution and the mixture was allowed to crystallize by diffusion at 0 °C. Aggregates of well-developped crystals which formed over several days were filtered off, washed with a small amount of diethyl ether, and dried under vacuum to afford **9** as a rusty orange crystalline solid (74.1 mg, 52%).

^1H NMR ($CDCl_3$): δ 2.79 (d, $^4J_{PH}$ = 2.9 Hz, 3 H, N*Me*), 2.85 (d, $^4J_{PH}$ = 2.7 Hz, 3 H, N*Me*), 3.43 (s, 3 H, O*Me*), 3.48 (d, $^2J_{HH}$ = 17.0 Hz, 1 H, CH_2CO_2), 3.99 (dd, $^2J_{HH}$ = 13.6, $^4J_{PH}$ = 2.4 Hz, 1 H, CH_2N), 4.04 (d, $^2J_{HH}$ = 17.0 Hz, 1 H, CH_2CO_2), 4.08 (dd, $^2J_{HH}$ = 13.6, $^4J_{PH}$. 2 Hz, 1 H, CH_2N), 4.20 (s, 5 H, C_5H_5), 4.47 (apparent td, 1 H, C_5H_3), 4.57, 4.62 (2H m, 1 H, C_5H_3), 6.11−8.14 (m, 14 H, aromatics). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 34.64 (d, $^3J_{PC}$ = 2 Hz, *C*H_2CO_2), 50.11, 50.42 (2H d, $^3J_{PC}$ = 2 Hz, N*Me*), 51.41 (O*Me*), 70.23 (d, J_{PC} = 8 Hz, *C*H C_5H_3), 71.13 (C_5H_5), 72.20 (d, $^1J_{PC}$ = 51 Hz, *C*-P C_5H_3), 72.74 (d, J_{PC} = 7 Hz, *C*H C_5H_3), 73.40 (d, $^3J_{PC}$ = 6 Hz, N*C*H_2), 75.85 (d, J_{PC} = 9 Hz, *C*H C_5H_3), 85.66 (d, $^2J_{PC}$ = 12 Hz, *C*-CH_2 C_5H_3), 121.94, 123.42 (*C*H C_6H_4), 124.70 (d, J_{PC} = 6 Hz, *C*H C_6H_4), 127.36 (d, J_{PC} = 10 Hz, *C*H PPh_2), 127.69 (d, J_{PC} = 11 Hz, *C*H PPh_2), 129.82, 130.27 (2H d, J_{PC} = 2 Hz, *C*H PPh_2), 133.52, 133.82 (2H d, $^1J_{PC}$ = 52 Hz, *C*-P PPh_2), 134.54 (d, J_{PC} = 11 Hz, *C*H PPh_2), 135.17 (d, J_{PC} = 13 Hz, *C*H PPh_2), 137.42 (d, J_{PC} = 10 Hz, *C*H C_6H_4), 147.56 (d, J_{PC} = 2 Hz, C_{ipso} C_6H_4), 152.29 (d, J_{PC} = 1 Hz, C_{ipso} C_6H_4), 171.82 (*C*O_2Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 28.0 (s). IR (Nujol; $\tilde{\nu}$/cm^{-1}) $\nu_{C=O}$ 1734 vs; 1579 m, 1246 m, 1193 w, 1168 s, 1147 m, 1107 m, 1098 m, 1018 m, 999 m, 973 w, 741 vs, 695 s, 509 m, 490 s, 473 m. Anal. Calcd for $C_{34}H_{35}ClFeNO_2PPd$: C, 56.85; H, 4.91; N, 1.95. Found: C, 56.46; H, 4.82; N, 2.07.

In Situ NMR Study of Bridge Cleavage in 7 with *rac*-Hpfa and 4. Compounds **7** (27.6 mg, 50 μmol) and **4** (44.3 mg, 0.10 mmol) were dissolved in $CDCl_3$ (0.8 mL), and the solution was transferred into an NMR tube and immediately analyzed by NMR spectroscopy. A subsequent evaporation afforded **9** as an orange foam in quantitative yield. A similar reaction of **7** with Hpfa (42.8 mg, 0.10 mmol) gave an intractable mixture.

Prepation of Bis(acetonitrile){2-[(dimethylamino)-methyl]phenyl-κ^2C^1,*N*}palladium(II) Perchlorate (11). A solution of silver perchlorate (207.6 mg, 1.00 mmol) in dry acetonitrile (5 mL) was added to a solution of complex **7** (276.2 mg, 0.50 mmol) in dichloromethane (10 mL). A white precipitate formed immediately. The mixture was stirred for 30 min at room temperature, precipitated AgCl was removed, and the filtrate was evaporated under reduced pressure. The residue was dissolved in acetonitrile (2 mL), diethyl ether was added to the solution as the top layer, and the mixture crystallized by liquid-phase diffusion at 0 °C for several days. The deposited crystalline solid was filtered off, washed with ether, and dried under reduced pressure to give **11** as colorless needles. Yield: 388.2 g, 92%.

^1H NMR ($CDCl_3$): δ 2.30, 2.49 (2H s, 3 H, *Me*CN), 2.85 (s, 6 H, NMe_2), 3.94 (2, 2 H, NCH_2), 6.87−7.07 (m, 4 H, C_6H_4). ^{13}C NMR ($CDCl_3$): δ 2.68, 3.52 (*Me*CN), 52.66 (NMe_2), 73.06 (NCH_2), 119.15, 120.56 (Me*C*N), 122.36, 125.83, 125.99, 133.35 (*C*H C_6H_4), 141.22, 147.05 (C_{ipso} C_6H_4). IR (Nujol; $\tilde{\nu}$/cm^{-1}) ν_{OH} 3386 s br; $\nu_{C\equiv N}$ 2332 m, 2318 m, 2304 m, 2291 m; 1636 m; $\nu_3(ClO_4)$ 1090 vs br composite; 848 m, 744 s, $\nu_4(ClO_4)$ 625 s; 505−529 m composite, 431 m. Anal. Calcd for $C_{13}H_{18}ClN_3O_4Pd$: C, 36.99; H, 4.30; N, 9.95. Found: C, 37.05; H, 4.21; N, 9.84.

Preparation of [*SP*-4-3]-{2-[(dimethylamino-κN)methyl]phenyl-κC^1}{*rac*-methyl [2-(diphenylphosphino-κP)-ferrocenyl]acetate-κO^2}palladium(II) Perchlorate (10). A solution of **4** (93.8 mg, 0.21 mmol) in dichloromethane (1 mL) was added to a solution of **11** (88.9 mg, 0.21 mmol) in the same solvent (2 mL). The resulting clear orange solution was allowed to stand for 90 min at room temperature, diethyl ether was added as the top layer, and the mixture was allowed to crystallize by diffusion at 0 °C. After several days, the separated crystals were filtered off, washed with diethyl ether, and dried under vacuum to afford **10** as an air-stable orange crystalline solid (121.4 mg, 74%).

^1H NMR ($CDCl_3$): δ 2.82 (d, $^2J_{HH}$ = 15.4 Hz, 1 H, CH_2CO_2), 2.87 (d, $^4J_{PH}$ = 2.1 Hz, 3 H, N*Me*), 3.08 (d, $^4J_{PH}$ = 3.4 Hz, 3 H, N*Me*), 3.35 (d, $^2J_{HH}$ = 15.4 Hz, 1 H, CH_2CO_2), 3.53 (m, 1 H, C_5H_3), 3.76 (dd, $^2J_{HH}$ = 13.8, $^4J_{PH}$ = 3.8 Hz, 1 H, CH_2N), 4.03 (s, 3 H, O*Me*), 4.32 (s, 5 H, C_5H_5), 4.39 (at, 1 H, C_5H_3), 4.51 (m, 1 H, C_5H_3), 4.67 (d, $^2J_{HH}$ = 13.8 Hz, 1 H, CH_2N), 6.26−7.87 (m, 14 H, aromatics). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 33.42 (*C*H_2-CO_2), 49.48 (d, $^3J_{PC}$ = 3 Hz, N*Me*), 50.68 (d, $^3J_{PC}$ = 2 Hz, N*Me*), 55.32 (O*Me*), 69.61 (*C*H C_5H_3), 70.88 (C_5H_5), 71.30 (d, $^3J_{PC}$ =

Table 4. Crystallographic Data and Data Collection and Structure Refinement Details

	2	**3**	*rac*-Hpfa	**5**
formula	$C_{32}H_{33}BrFeNP$	$C_{24}H_{20}FeNP$	$C_{24}H_{21}FeO_2P$	$C_{24}H_{21}FeO_3P$
M_r	598.32	409.23	428.23	444.23
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	37.3525(7)	9.0732(2)	15.3279(3)	9.4619(2)
b (Å)	12.1050(2)	10.4864(2)	8.0463(1)	19.5101(3)
c (Å)	12.7497(2)	11.3251(2)	16.4122(3)	11.1031(2)
α (deg)	90	100.2220(1)	90	90
β (deg)	101.5488(9)	111.7990(1)	93.523(1)	105.952(1)
γ (deg)	90	96.6800(1)	90	90
V (Å^3)	5648.1(2)	964.82(3)	2020.34(6)	1970.73(6)
Z	8	2	4	4
D_c (g mL^{-1})	1.407	1.409	1.408	1.497
μ(Mo Kα) (mm^{-1})	2.027	0.872	0.842	0.870
T_{min}, T_{max}[e]	0.694, 0.862	not corrected	not corrected	not corrected
θ_{max} (deg)	27.5	27.5	27.5	27.5
data completness (%)	99.8	99.2	99.7	99.6
total no. of diffrns	44699	17702	35075	34753
no. of unique/obsd[a] diffrns	6747/5547	4392/4102	4634/3875	4507/4074
R_{int} (%)[b]	3.14	1.83	3.36	1.79
no. of params	327	244	257	262
R (obsd diffrns) (%)[c]	2.90	2.57	3.24	3.80
R, R_w (all data) (%)[c]	3.85, 7.11	2.84, 6.69	4.39, 8.35	4.25, 10.23
S (all data)[d]	1.04	1.05	1.05	1.05
$\Delta\rho$ (e Å^{-3})	0.37, −0.49	0.33, −0.37	0.50,[f] −0.37	0.77, −0.66

	6	**8**	**9**	**10**
formula	$C_{24}H_{21}FeO_2PS$	$C_{33}H_{32}FeNO_2PPd$	$C_{34}H_{35}ClFeNO_2PPd$	$C_{34}H_{35}ClFeNO_6PPd$
M_r	460.29	667.82	718.30	782.30
cryst syst	triclinic	monoclinic	orthorhombic	monoclinic
space group	$P\bar{1}$ (No. 2)	*C*2/c (No. 15)	*Pbca* (No. 61)	$P2_1/c$ (No. 14)
a (Å)	8.3270(2)	34.0896(4)	10.2801(1)	17.1227(2)
b (Å)	11.6610(3)	8.8138(1)	18.2507(1)	11.5599(1)
c (Å)	11.7886(2)	18.7679(2)	32.1378(3)	17.3407(2)
α (deg)	99.275(1)	90	90	90
β (deg)	107.325(1)	101.5033(5)	90	108.3949(7)
γ (deg)	104.689(1)	90	90	90
V (Å^3)	1021.73(4)	5525.7(1)	6029.66(9)	3256.98(6)
Z	2	8	8	4
D_c (g mL^{-1})	1.496	1.409	1.583	1.595
μ(Mo Kα) (mm^{-1})	0.937	0.872	1.252	1.175
T_{min}, T_{max}[e]	not corrected	0.717, 0.758	0.741, 0.832	0.661, 0.708
θ_{max} (deg)	27.5	27.5	27.5	30.0
data completness (%)	98.7	99.7	99.8	99.7
total no. of diffrns	17 711	40 820	100 918	66 759
no. of unique/obsd[a] diffrns	4644/4324	3618/5793	6907/5360	9519/8619
R_{int} (%)[b]	1.60	3.04	5.71	3.04
no. of params	266	354	373	409
R (obsd diffrns) (%)[c]	2.60	2.26	3.32	2.60
R, R_w (all data) (%)[c]	2.85, 6.34	2.57, 5.29	5.01, 7.78	3.02, 6.32
S (all data)[d]	1.05	1.05	1.08	1.06
$\Delta\rho$ (e Å^{-3})	0.31, −0.37	0.46, −0.61	0.86, −0.97	0.67, −0.80

[a] Diffractions with $|F_o| > 4\sigma(F_o)$. [b] $R_{int} = \sum|F_o^2 - F_{o,mean}^2|/3F_o^2$. [c] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$, $wR(F^2) = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum w(F_o^2)^2]^2$. [d] $S = [\sum\{w(F_o^2 - F_c^2)^2\}/(N_{diffrns} - N_{params})]^2$. [e] Transmission coefficient range. [f] A maximum due to the lone electron pair at the phosphorus atom.

4 Hz, NCH_2), 72.04 (d, $^1J_{PC}$ = 56 Hz, *C*-P C_5H_3), 74.04 (d, J_{PC} = 4 Hz, *C*H C_5H_3), 76.45 (d, J_{PC} = 7 Hz, *C*H C_5H_3), 82.11 (d, $^2J_{PC}$ = 15 Hz, *C*-CH_2 C_5H_3), 122.48, 125.27 (*C*H C_6H_4), 125.91 (d, J_{PC} = 6 Hz, *C*H C_6H_4), 126.65 (d, $^1J_{PC}$ = 46 Hz, *C*-P PPh_2), 128.41 (d, $^1J_{PC}$ = 58 Hz, *C*-P PPh_2), 128.41 (d, J_{PC} = 12 Hz, *C*H PPh_2), 129.49 (d, J_{PC} = 11 Hz, *C*H PPh_2), 131.41, 132.45 (2H d, J_{PC} = 2 Hz, *C*H PPh_2), 133.55 (d, J_{PC} = 12 Hz, *C*H PPh_2), 135.65 (d, J_{PC} = 14 Hz, *C*H PPh_2), 138.31 (d, J_{PC} = 13 Hz, *C*H C_6H_4), 141.42 (d, J_{PC} = 3 Hz, C_{ipso} C_6H_4), 147.57 (d, J_{PC} = 2 Hz, C_{ipso} C_6H_4), 179.05 (CO_2Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.8 (s). IR (Nujol; $\tilde{\nu}$/cm^{-1}): $\nu_{C=O}$ 1672 vs; 1581 m, 1355 s, 1268 s, 1181 m, $\nu_3(ClO_4)$ 1100 vs, 1090 vs composite; 893 m, 867 m, 843 s, 828 s, 747 s, 700 s, 693 s, 688 s, $\nu_4(ClO_4)$ 624 s; 543 m, 534 s, 500 s, 486 m, 471 m. Anal. Calcd for $C_{34}H_{35}ClFeNO_6PPd$: C, 52.20; H, 4.51; N, 1.79. Found: C, 52.23; H, 4.43; N, 2.02.

Direct Conversion of 7 into 10. A mixture of **7** (13.8 mg, 25 μmol) and **4** (22.2, 50 μmol) was dissolved in chloroform (1 mL). After this mixture stood for 5 min, a solution of $AgClO_4$ (11.2 mg, 54 μmol) in acetonitrile (0.5 mL) was added, causing an immediate separation of AgCl as a white precipitate. The mixture was stirred for 10 min, all volatiles were removed under reduced pressure, and the residue was extracted with dichloromethane (3 × 0.5 mL). The extracts were filtered, and the product was crystallized by liquid-phase diffusion of hexane over several days at 0 °C. Fine, yellow-orange microcrystals of **10** that formed after several days were filtered off, washed with a small amount of diethyl ether, and dried in air. Yield: 35.2 mg (90%). The product was characterized by NMR spectroscopy.

X-ray Crystallography. X-ray-quality crystals were obtained by recrystallization from hot glacial acetic acid (**3**, orange prism, 0.18 × 0.30 × 0.45 mm^3) and hot aqueous (ca. 80%) acetic acid (Hpfa, orange plate, 0.05 × 0.20 × 0.30 mm^3), by liquid-phase diffusion of hexane into an ethyl acetate solution (**5**, orange plate, 0.15 × 0.35 × 0.40 mm^3), from

methanol (**6**, orange prism, 0.15 × 0.25 × 0.45 mm^3), by liquid-phase diffusion of hexane into dichloromethane solution (**10**, orange prism, 0.30 × 0.33 × 0.40 mm^3), or directly from the reaction batch (**2**, orange brown plate, 0.08 × 0.30 × 0.35 mm^3; **8**, rusty orange block, 0.23 × 0.25 × 0.25 mm^3; **9**, orange block, 0.15 × 0.23 × 0.25 mm^3). Full-set diffraction data ($\pm h$, $\pm k$, $\pm l$) for all compounds were collected on a Nonius Kappa CCD diffractometer equipped with a Cryostream Cooler (Oxford Crysoystems) at 150 K using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) and analyzed with the HKL program package[37] (Table 4). The data for **2** and complexes **8**−**10** were corrected for absorption by an empirical method incorporated in the diffactometer software (SORTAV routine).

All structures were solved by direct methods (SIR92[38]) and refined by weighted full-matrix least squares on F^2 (SHELXL97[39]). The final geometric calculations were carried out with a recent version of the Platon program.[40] All non-hydrogen atoms were refined with anisotropic thermal motion parameters. Carboxyl hydrogen atoms in Hpfa and **6** were identified on difference electron density maps and isotropically refined. The acidic hydrogen in **5** was found as well, but since an analogous refinement proved unstable, it was fixed in the position revealed by the difference electron density map. All other hydrogen atoms were included in the calculated positions (C−H bond lengths: 0.93 Å (aromatic), 0.97 Å (methylene), and 0.96 Å (methyl)) and assigned $U_{iso}(H) = 1.2[U_{eq}(C)]$ (aromatic and methylene) or $1.5[U_{eq}(C)]$ (methyl). CCDC reference numbers: 194136−194143 (for **2**, **3**, *rac*-Hpfa, **5**, **6**, and **8**−**10**, respectively).

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Supporting Information Available: Drawings of the molecular structures for **3**, **5** and **6**, full listings of the refined atomic coordinates, anisotropic thermal motion parameters, calculated hydrogen coordinates, bond distances and bond angles, dihedral angles subtended by the selected least-squares planes, and summaries of shortest intermolecular interactions, and packing diagrams for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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